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Influence of structural disorder on magnetic order: An *ab initio* study of amorphous Fe, Co, and Ni

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The magnetic order in amorphous Fe, Co, and Ni is studied *ab initio* within the framework of density-functional theory and the local-spin-density approximation using the linear-muffin-tin-orbital method in the atomic-sphere approximation. Noncollinear magnetic structures are treated in a fully self-consistent manner for rather small supercells containing 16 atoms. The results for iron show that noncollinear structures are energetically lower than collinear ones at a density of 8.4 g/cm^3 and energetically equivalent at a density of 7.9 g/cm^3. At a density of 7.4 g/cm^3 amorphous iron remains ferromagnetic. Cobalt and nickel remain ferromagnetic upon structural disordering at the densities of the corresponding dense packed crystalline structures.

Magnetism in amorphous transition-metal alloys is of great interest from both fundamental and technological points of view. The most fundamental question is whether or not the magnetic order will be changed by structural disorder. The answer to this question is quite controversial. Extrapolations of the magnetic behavior of amorphous Fe-rich $\mathrm{Fe}_{1-c}\mathrm{Zr}_c$ alloys to pure amorphous Fe lead to the prediction of a spin-glass behavior[1,2] or an asperomagnetic behavior,[3] whereas in thin films of amorphous iron in Y/Fe/Y layered structures no indications for a spin-glass behavior was found.[4] Theoretically, Kakehashi[5] and Yu and Kakehashi[6] predicted by a degenerate-band Hubbard model a spin-glass ground state for amorphous iron and a ferromagnetic ground state for cobalt. For amorphous Ni they found a paramagnetic ground state (with local moments), but they stated that the results depend sensitively on the choice of the input parameters and that therefore *ab initio* calculations are required. Turek and Hafner[7] did a thorough investigation of amorphous iron and cobalt with spin-polarized *ab initio* linear-muffin-tin-orbital calculations (LMTO), using a supercell approach, with a supercell consisting of 64 atoms. But because in usual spin-polarized band structure calculations only the longitudinal component of spin moments is considered, they could not observe a canted magnetic structure directly. They found for densities below 7.5 g/cm^3 an inhomogeneous ferromagnet, and then upon compression more and more sites acquire a negative magnetic moment until at 9.5 g/cm^3 a broad distribution of magnetic moments with zero net magnetization, i.e., a random collinear state is obtained. Upon further compression a transition to a nonmagnetic state occurred. Bratkovsky and Smirnov[8] performed *ab initio* calculations with the real-space tight-binding LMTO method (but did also not allow for spin canting). This allows the use of a recursion method to calculate the band structure, which enables one to consider large amorphous clusters consisting of several hundred atoms. Self-consistency is obtained only for an average atom, whereas in a supercell calculation all atoms are treated locally self-consistently. For amorphous Fe a ferromagnetic state with no tendency to form a spin-glass state was found. One reason for the discrepancy between this result and the one of Turek and Hafner[7] might be that the calculation of Bratkovsky and Smirnov overestimates the stability due to the use of an average instead of a local self-consistency. Krey, Krauss, and Krompiewski[9] performed tight-binding calculations on amorphous iron based on the empirical Slater-Koster parametrization and a Hubbard-type mechanism with a fitted value of the interaction parameter to generate the spin polarization for a supercell consisting of 54 atoms which then was repeated periodically. They found canted magnetic structures, either asperomagnetic or speromagnetic to be the energetically lowest states, both for a density of 7.39 g/cm^3 as well as for 9.19 g/cm^3. Lorenz and Hafner[10] also performed calculations based on the tight-binding Hubbard Hamiltonian. Instead of using a purely empirical parametrization they obtained spin-averaged transfer integrals from a tight-binding LMTO calculation[11] for the random collinear structure, assuming that the transfer integrals constructed for this reference system are well transferable to noncollinear configurations. The interaction parameter was identified with the Stoner parameter I which is the factor of proportionality between the local exchange splitting and the local magnetic moment which they found in their LMTO calculation. They obtained at a density of 7.5 g/cm^3 an asperomagnetic state and at densities of 7.9 and 8.4 g/cm^3 speromagnetic states.

In this work we present results of *ab initio* calculations which take into account noncollinear spin arrangements in a fully self-consistent manner, that means that we calculate the full spin-density matrix without any restriction on the direction of the local spin polarization, i.e., we obtain the absolute values and the directions of local magnetic moments. We studied supercells of structurally disordered iron, cobalt, and nickel, each consisting of 16 atoms. We generated our structurally disordered samples by static relaxation of a random structure, using pair potentials as given by Brandt and Kronmüller[12] for Fe. The same structural models for Fe, Co, and Ni were used in order to study the influence of the chemical effect upon increasing the number of d electrons. To treat noncollinear magnetic structures we adopted the method of Kübler and co-workers,[13,14] which we implemented within the framework of the LMTO method in the atomic-sphere approximation.[15,11] The number of atoms in our supercell is limited by the calculational effort and is smaller than that in other *ab initio* calculations. The reason is that the numerical effort when considering noncollinear spin arrangements is four times higher than in conventional spin polarized calculations for each iteration step, that a relative large number of iteration steps is required to achieve self-consistency, and that one has to use several sets of starting parameters for the iteration process. Because of the small number of atoms within our supercells we only can study the effect of structural disorder on a small scale and we cannot claim to have investigated realistic amorphous systems.

To make calculations feasible, even for small supercells, one has to overcome two numerical difficulties within the iteration process to self-consistency. The first one is a slow convergence rate with respect to the directions of magnetic moments, the second one arises from the fact that there may be many metastable states with energies higher than the one of the ground state. The first difficulty can be overcome by using "good" starting points in the configurational hyperspace, which now comprises not only the absolute value but also the direction of each local magnetic moment. As a matter of fact, numerical convergency with respect to the direction of moments is much slower than with respect to their magnitude. This is because the energy gain when rotating a local magnetic moment is determined by the interatomic exchange interactions, which may be competing with each other, whereas the absolute value of the magnetic moment is mainly determined by the much stronger intra-atomic exchange interaction. This necessitates a careful choice of the initial directions of the magnetic moments when starting the self-consistency cycle. We obtain such starting points in the configurational hyperspace by the following procedure. At first, we try to get a feeling for the exchange couplings (sign and relative values) between all sites in our sample by doing a series of one-shot calculations, where we put at just one atomic site a magnetic moment of $1.0\mu_B$, for instance, in an otherwise nonmagnetic matrix, determine with one iteration step (starting from the self-consistent nonmagnetic solution) the sign and magnitude of the induced moments at other atomic sites and take them as proportional to the exchange coupling to the site where we have put the moment. If doing such a calculation with "test moments" for all sites, respectively, we obtain an estimate for all exchange couplings within our sample. These estimates are then used in a Heisenberg model with moments of fixed identical length at each atomic site, and for this model stable directional configurations where the torque acting on the moments vanishes are determined. We do this for typically 500 randomly generated starting configurations and obtain by this procedure several different types of stable directional configurations, e.g., nearly antiferromagnetic and strongly noncollinear ones. These directional configurations differ in their interatomic exchange energy of the above discussed Heisenberg model, and we use configurations of lower and medium energy as starting points for our *ab initio* calculation. The question is how well the magnetic part of the real system with the orientation of the magnetic moments fixed according to these directional configurations is represented by the interatomic exchange energy of the Heisenberg model. In reality the magnitude of the local magnetic moments will depend on the local orientation, and the magnetic part of the energy is given by the competition between the interatomic exchange energy responsible for the relative orientations of the moments and the intra-atomic exchange energy related to the magnitudes of the moments. Whereas our Heisenberg model is just able to give an estimate for the interatomic part, both contributions are accounted for in an *ab initio* calculation. As a result, when using the stable directional configurations as obtained from the Heisenberg model as starting configurations for the *ab initio* calculation, we should not consider just the energetically lowest Heisenberg configuration but we should sample a variety of different starting configurations. We thereby found that those starting configurations for which many interatomic couplings are frustrated either will lead to a self-consistent configuration of high total energy or even will not yield convergence of the self-consistency cycle. For the other starting configurations self-consistency with respect to the total energy and the magnitude and the orientation of the magnetic moments is then obtained within about 50 iteration steps. The second problem we mentioned above is that there most probably will be many metastable states, so that we will arrive at different self-consistent solutions when starting at different points and it is by no means guaranteed that we can find the real ground state solution. This problem cannot be overcome in general, because we never can exclude that there is no other canted spin structure with lower energy than the spin structure we found in our self-consistency cycle. The only question which we can definitely answer is whether there are noncollinear spin structures with lower energies than the ferromagnetic structure. On the other hand, if via our procedure to estimate the exchange couplings there is no hint of competing exchange interactions, i.e., all induced moments are parallel, we think this to be a clear indication that the ferromagnetic structure is most stable.

If one regards the amorphous structure as being similar to the cubic face centered one with respect to the arrangement of nearest neighbors but with varying interatomic distances, it is just on hand first to look at the density dependence of the magnetic order in iron, cobalt, and nickel in the fcc structure. For fcc cobalt and nickel, the ferromagnetic structure is the only stable one (see Refs. 16 and 17) and we found that it is stable for densities from lower ones to up to at least 1.5 times the equilibrium density. Therefore one can expect that the ferromagnetic order will be stable upon structural disordering in cobalt and nickel. On the other hand, in fcc iron there are several known stable spin-configurations, ferromagnetic, antiferromagnetic, and at least three noncollinear ones (for details see Ref. 18), their stability depending sensitively on the density. Therefore one can expect a very complicated situation in amorphous iron, where interatomic distances vary. The existence or nonexistence of noncollinear magnetic states can be connected to the fact that cobalt and nickel are "strong" ferromagnets in the sense that the spin-majority band is completely filled whereas iron is a weak ferromagnet, that means that both, the spin-majority and the spin-minority band, contribute to the density of states at the Fermi level. This makes it energetically easy to hybridize spin-up and spin-down states, i.e., to induce a noncollinear magnetic structure. In a strong ferromagnet, on the other hand, it costs much energy to bring up a spin-majority electron from its state below the Fermi level up to the Fermi level before hybridization with spin-minority states can occur.

TABLE I. Results for the magnetic structure of structurally disordered iron at the three considered densities. The data given are the energetically lowest configuration(s) and the local magnetic moments per atom for these configurations and in brackets the energetically second-lowest configuration and the energy difference per atom to the lowest configuration.

	Structural model 1	Structural model 2
7.4 g/cm^3	ferromagnetic 2.6μ_B (smeared 90°, 64 meV)	
7.9 g/cm^3	ferromagnetic and smeared 90° ferromagn.: 2.4μ_B smeared 90°: 1.9μ_B (statistical distr., 13 meV)	smeared 90° 1.9μ_B (statistical distr., 22 meV)
8.4 g/cm^3	smeared 90° 1.6μ_B (statistical distr. and random collin., 6 meV)	smeared 90° 1.5μ_B (random collin., 6 meV)

We calculated the magnetic structure in iron at three densities. The first one was 7.4 g/cm^3, which is about the density of ficticious amorphous iron. In fcc iron at this density the noncollinear and the ferromagnetic configuration have almost the same energy. The second density we considered was 7.9 g/cm^3, which is about the equilibrium density of bcc iron and is the one where in fcc iron ferromagnetic and antiferromagnetic configurations are nearly energetically equivalent but the noncollinear ordering is of lower energy. The third density was 8.4 g/cm^3, in fcc iron at this density antiferromagnetic and noncollinear spin ordering are almost equivalent and a ferromagnetic order does not exist. Our results for the structurally disordered samples are compiled in Table I. The structural model 1 has a somewhat higher degree of disorder than the structural model 2. We found two types of noncollinear spin structures, "statistical configurations" (i.e., speromagnetic) and "smeared-90° configurations," examples for each type are given in Fig. 1. In Fig. 2 we give the angular distribution of moments in a $\cos\theta$-$\phi/2\pi$ coordinate system where in the left (right) graph the data correspond to those presented in Fig. 1, upper (lower) part. According to Table I, the ferromagnetic configuration bears much larger magnetic moments than the noncollinear configurations, i.e., it is stabilized by the intra-atomic exchange interactions whereas the noncollinear configurations are induced by the interatomic exchange interactions on the cost of intra-atomic exchange energy. It becomes obvious from Table I that as a result of structural disordering the relative stability of the ferromagnetic configuration is increased as compared to fcc iron, and the noncollinear structures become energetically favorable only at our highest density where the ferromagnetic configuration is unstable. The energetically low-lying noncollinear configurations thereby are of "smeared-90° type" rather than statistically random (i.e., speromagnetic). In contrast to Krey, Krauss, and Krompiewski[9] and Lorenz and Hafner[10] we never found asperomagnetic structures. One reason for this discrepancy might be that we used rather small supercells which possibly do not properly describe a real amorphous system. A second reason might be that for the case of iron where there is a highly delicate balance between inter- and intra-atomic interactions creating competing spin configurations even for the fcc phase the transferability of the tight-binding parameters to situations with different spin configurations is not guaranteed (see discussion above). The average absolute value of the local magnetic moment of the noncollinear states agrees well with the *ab initio* results of Turek and Hafner[7] for their random collinear state and the one found by Bratkovsky and Smirnov[8] but is about three times larger than the one found by Krey, Krauss, and Krompiewski[9] for the speromagnetic

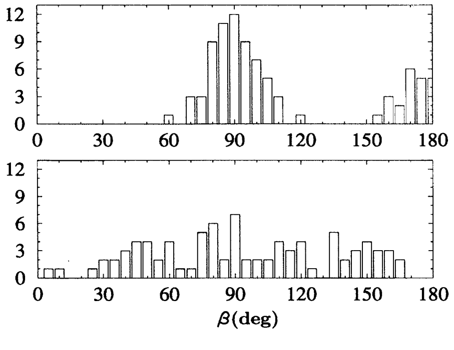

FIG. 1. Distribution of relative angles β between neighboring magnetic moments in structurally disordered iron. Upper graph: smeared-90° configuration, lower graph: statistical configuration.

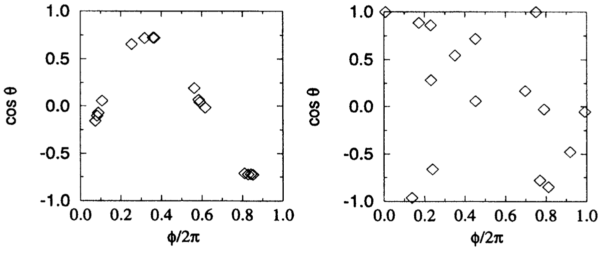

FIG. 2. Angular distribution of the local magnetic moments in structurally disordered iron. Left graph: smeared-90° configuration, right graph: statistical configuration. Both graphs display the same data as in Fig. 1.

states. The difference may arise because the exchange splitting between the spin-up and spin-down states at each atom is an external parameter in the semiempirical calculation of Krey, Kraus, and Krompiewski[9] but it is determined self-consistently in the *ab initio* calculations. The energy differences between our energetically lowest and second-lowest configurations are of the order of 10 meV per atom (see Table I). We therefore do not expect that the local anisotropy energy due to spin-orbit coupling which is about 0.4 meV per atom[19] has an influence on the qualitative behavior.

For structurally disordered cobalt we considered only one atomic configuration at a density of hcp cobalt (8.89 g/cm^3). From all the spin configurations which we obtained the ferromagnetic configuration was the lowest in energy, with a very sharp distribution of the absolute values of the local magnetic moments with an average of $1.65\mu_B$ and a maximum deviation from this average value of $0.05\mu_B$. This agrees very well with the findings of Turek and Hafner[7] and with the results of Kakehashi.[5]

For structurally disordered nickel we considered again only one sample at the density of fcc nickel (8.91 g/cm^3). The energetically lowest magnetic structure was ferromagnetic with an average value of $0.64\mu_B$ for the local magnetic moment. The distribution of the absolute values of the moments was very sharp, similar to the results of cobalt. Our result sheds some light onto the question whether the ferromagnetic state of nickel is stable upon structural disorder or will transform into a paramagnetic state. This question could not be settled by the calculation of Kakehashi.[5]

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